PATENT ABSTRACTS OF JAPAN

(11)Publication number : **09-169897**
(43)Date of publication of application : **30.06.1997**

(51)Int.Cl. **C08L 67/04**
C08G 63/16

(21)Application number : **07-348248**
(22)Date of filing : **19.12.1995**

(71)Applicant : **UNITIKA LTD**
(72)Inventor : **MUKAI KATSUYUKI**
YAMADA YOSHIHISA
SAWARA TETSUYA

(54) BIODEGRADABLE FIBER REINFORCED MOLDING AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a biodegradable fiber reinforced molding that has sufficient strength during a period within which an object is to be realized, is decomposed in the natural environment after achieving the object and is excellent in heat resistance by using biodegradable reinforcing fibers.
SOLUTION: This biodegradable fiber reinforced molding in which 5-500 pts.wt. highly heat-resistant biodegradable reinforcing fibers having a mean length of 1-50mm are bonded in a dispersed state to 100 pts.wt. aliphatic polyester resin. It is obtained by dispersing 100 pts.wt. aliphatic polyester powder and/or fibers and 5-500 pts.wt. highly heat-resistant biodegradable reinforcing fibers having a mean length of 1-50mm, preferably together with a binder, in a liquid medium, removing the liquid medium to form a sheet, drying the sheet, heating it at a temperature above the melting point of the polyester and compressing it. Examples of highly heat-resistant biodegradable reinforcing fibers used include natural fibers, regenerated fibers and polyvinyl alcohol fibers.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to a biodegradable fiber strengthening Plastic solid which consists of matrix resin which has biodegradability, and a fiber reinforced which has biodegradability, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]Although the raw material disassembled in natural environment is demanded to the environmental problem in a terrestrial scale in recent years, When the natural fiber represented by cotton, hemp, etc. was laid underground into the ground etc., it changed with textiles to be used, but when it was early, decomposition started in about two weeks, intensity fell and it passed half a year also, there was a fault in which most disappears.
[0003]Therefore, since strength reduction happens before achieving the purpose of use when a natural fiber is used under environment, such as inside of the ground, and underwater, the use under such conditions is not used for the field for which restriction is received, especially the stability over a long period of time is needed. Although synthetic fibers, such as aromatic polyester and nylon, are used for such a field, since it is not remained and decomposed into the inside of the ground, or underwater after a long period of time where shape is held when used by the inside of the ground, underwater, etc., these synthetic fibers may cause a big environmental problem.
[0004]On the other hand, since the melting point and mechanical properties were low as compared with aromatic polyester, such as polyethylene terephthalate, aliphatic polyester had being observed [little] until now. However, development of the polymers raw material disassembled in natural environment comes to be demanded to the environmental problem in a terrestrial scale in recent years, and are cheap also in it, And it has a great hope as a biodegradable material which can substitute a general-purpose plastic for the aliphatic polyester which can be supplied in large quantities.
[0005]As aliphatic polyester manufactured by melt polycondensation with alpha, omega-aliphatic series diol and alpha, and omega- aliphatic dicarboxylic acid, Polyethylene succinate, polybutylene succinate, a polybutylene horse mackerel peat, etc. are the polymer known for many years, and if it lays underground into soil, it is checked that biodegradation is carried out by the microorganism.
[0006]
[Problem(s) to be Solved by the Invention]However, although polybutylene succinate and polyethylene succinate are mentioned as what has the melting point comparatively high also in it although these aliphatic polyester has the low melting point as mentioned above, In polybutylene succinate, around 118 ** and polyethylene succinate of the melting point are still around 104 **. Also in other aliphatic polyester, since the melting point is low, compared with the general-purpose resin etc. which are used now, it is

generally inferior in respect of heat resistance etc. Since mechanical properties, such as tensile strength and elongation after fracture, were low, there was a fault in which the use is restrained.
[0007][within the period when this invention cancels the above problems in and the purpose of use should be achieved], It aims at providing the biodegradable fiber strengthening Plastic solid which had sufficient intensity, was disassembled even into carbon dioxide and water in natural environment after achieving the purpose of use, did not give load to natural environment, and excelled the case where it was an aliphatic polyester simple substance in heat resistance.
[0008]
[Means for Solving the Problem]A biodegradable fiber strengthening Plastic solid, wherein this invention attains said purpose and 1-50 mm of mean fiber length's five to biodegradable fiber 500 weight section for strengthening has combined it with aliphatic-polyester-resin 100 weight section by a dispersion state, And aliphatic polyester powder and/or textiles 100 weight section, and 1-50 mm of mean fiber length's five to biodegradable fiber 500 weight section for strengthening are distributed in a fluid medium, Subsequently, this fluid medium is removed, a sheet is formed, and let a manufacturing method of a biodegradable fiber strengthening Plastic solid carrying out heating compression molding at temperature more than the melting point of aliphatic polyester be a gist after making it dry.
[0009] [Embodiment of the Invention]Hereafter, this invention is explained in detail. This invention is characterized by a biodegradable fiber strengthening Plastic solid comprising the following.
Thermoplastic aliphatic polyester resin.
The heat-resistant high biodegradable fiber for strengthening.
[0010]As aliphatic polyester used for this invention, the following are mentioned as an example. Poly (alpha-hydroxy acid) or these copolymers, such as polyglycolic acid and polylactic acid, Poly, such as poly (epsilon-caprolactone) and poly (beta propiolactone) (omega-hydroxy alkanoate), Poly (3-hydroxy butyrate), poly (3-hydroxy BARIRETO), Microbiologic production polyester, such as poly (beta-hydroxy alkanoate), such as poly (3-hydroxy KAPURO rate), poly (3-hydroxy heptanoate), and poly (3-hydroxy octanoate), and poly (4-hydroxy butyrate), etc. are mentioned.
[0011]As what is obtained by the polycondensation of glycol and aliphatic dicarboxylic acid, Polyethylene succinate, polybutylene succinate, polyhexamethylene succinate, Polyethylene adipate, a polybutylene horse mackerel peat, a polyhexamethylene horse mackerel peat, Polyethylene oxalate, polybutylene oxalate, poly neopentyl oxalate, polyethylene sebacate, polybutylene sebacate, polyhexamethylene sebacate, etc. are mentioned. These may be two sorts or a copolymer beyond it, and as long as they make these the main ingredients, they may also contain other ingredients, for example, aromatic dicarboxylic acid, a polyfunctional hydroxyl group, carboxylic acid, etc. The aliphatic series polyester amide which is a copolymer of said aliphatic polyester and the aliphatic polyamide represented by nylon is also mentioned.
[0012]As a heat-resistant high biodegradable fiber for strengthening used for this invention, Cotton, flax, a ramie, ******, a hemp, hemp of Manila, kapok, pulp, Regenerated fiber, such as natural fibers, such as wool and silk, or viscose rayon, Bemberg rayon, polynosic rayon, and solvent spinning rayon, vinylons, or such mixed use articles are mentioned.
[0013]The mixture ratio of aliphatic polyester and the biodegradable fiber for strengthening in this invention needs to be five to biodegradable fiber textiles 500 weight section for strengthening to aliphatic polyester 100 weight section, and is 20 to 200 weight section especially preferably ten to 300 weight section preferably. It is difficult to give intensity whose mixture ratio of a biodegradable fiber is sufficient to aliphatic polyester 100 weight section in the case of less than five weight sections, and in exceeding 500 weight sections, it becomes difficult for processability to acquire the Plastic solid which is equal to use by worsening.
[0014]The biodegradable fiber strengthening Plastic solid of this invention can be manufactured, for example by the following methods. First, aliphatic polyester 100 weight section and five to biodegradable fiber 500 weight section for strengthening are made to distribute underwater. Thereby, the biodegradable fiber for strengthening will be in the state of composite-izing distributed uniformly into aliphatic polyester.
[0015]As for the particle diameter of the aliphatic polyester powder used here, it is desirable that it is 1 mm or less, the uniform dispersion of resin is possible in especially this range, and a uniform Plastic solid is acquired. As for the mean fiber length of aliphatic polyester textiles, it is desirable that it is 50 mm or less, it is easy to distribute in a fluid medium especially in this range, and a uniform Plastic solid is acquired.
[0016]As mean fiber length of the aforementioned biodegradable fiber for strengthening, a 1-50-mm thing is used and 3-25 mm is especially preferred. When it is in the tendency for intensity to fall when mean fiber length is shorter than 1 mm and exceeds 50 mm, the homogeneity of textiles and matrix resin is hard to tend be obtained. A 2-100-micrometer thing is used and, as for the mean fiber diameter of the textiles for strengthening, 5-50 micrometers is especially preferred. It is in the tendency for efficient removal of the fluid medium in the manufacturing method of this invention and desiccation to become difficult in the case of 2 micrometers or less, and, in the case of not less than 100 micrometers, is at the tendency for a uniform dispersion state to be hard to be acquired.
[0017]When making aliphatic polyester and the biodegradable fiber for strengthening distribute underwater and composite-izing, it is preferred to use a binding material for example, it is preferred to make a binding material add 0.1 to 10% of the weight by a part for a solid to the sheet obtained, and it is preferred to make it add 0.2 to 5% of the weight especially. Sulfonium salt, an isothio URONIUMU group united, for example as such a binding material, A pyridinium group, a quaternary ammonium group, a sulfate group, The polymeric latex which has the united negative ion or positive ion electric charge like acrylic polymer, or the styrene / butadiene polymer containing a sulfonate group or a carboxylate group and which becomes water from insoluble organic polymer

substantially is mentioned. In addition, starch including starch especially natural starch or line starch like cornstarch, and the starch containing positive ion starch that denaturalized enzymatically or chemically, etc. are suitable as a binding material.
[0018]When distributing aliphatic polyester and the biodegradable fiber for strengthening and composite-izing, It is preferred to use an organic coagulant and as such an organic coagulant, Various organic coagulants, such as aluminum polychloride (aluminum hydronalium oxychloride), polyacrylamide hydrolyzed in part, denaturation positive ion polyacrylamide. and diaryldiethyl ammonium chloride, are mentioned. Three or less % of the weight of the biodegradable fiber strengthening Plastic solid of the addition of this flocculating agent is preferred, and 1 or less % of the weight is preferred for it.
[0019]In addition, viscosity controlling agents, such as xanthene rubber, can also be used in order to adjust the viscosity of the slurry which distributed aliphatic polyester and the textiles for strengthening underwater.
[0020]Thus, underwater, distribution and after composite-izing, a sheet is formed for aliphatic polyester and the biodegradable fiber for strengthening. It is desirable to carry out solid liquid separation to shaping of a sheet so that an underwater solid may be desirably made with a sheet shaped in the way of paper making using a paper machine etc. After drying the obtained damp sheet, hot press is carried out in the state of the sheet-shaped voice of one sheet, or the layered product of two or more sheets. At this time, as a temperature at the time of carrying out hot press, it is preferred that it is higher than the melting point of aliphatic polyester as matrix resin 10-50 **, and it is preferred as a pressure that it is 5-100kg/cm2. Although after hot press is cooled by various kinds of means, it is hot press and power at the same pressure, and it is desirable to perform a cooling press at the temperature of 10-50 **.
[0021]Thus, although the biodegradable fiber strengthening Plastic solid of this invention is acquired, In acquiring the Plastic solid of shape other than a sheet shaped, after preheating beforehand the sheet which does not perform said hot press, the method of carrying out a cold press using a metallic mold or the method of carrying out a hot melt press using a metallic mold can be used. As for the preheat temperature in this case, or the temperature of a hot melt press, it is [more than the melting point of aliphatic polyester] preferred that it is 250 ** or less.
[0022]Since the high biodegradable fiber for strengthening of 1-50 mm of mean fiber length's heat resistance has combined the biodegradable fiber strengthening Plastic solid of this invention by the dispersion state in aliphatic polyester resin, While the intensity and heat resistance which were the faults of aliphatic polyester resin improve remarkably, controlling the ease of the decomposition which is a general fault of the heat-resistant high biodegradable fiber for strengthening -- use -- the time -- carrying out -- underwater and the inside of the ground -- laying underground -- having -- even if -- the purpose of use -- achieving -- it should have -- a period -- inside -- setting -- sufficient intensity -- being shown -- ******** . Since both aliphatic polyester resin and the biodegradable fiber for strengthening are biodegradability, after achieving the purpose of use, it is decomposed even into carbon dioxide and water in natural environment, and they do not give load to natural environment.
[0023] [Example]Hereafter, an example explains this invention concretely.
After adding the xanthan gum 0.25g, agitating in 17.5 l. of example 1 water, as textiles for strengthening, 87.5 g of hemp fibers (made in China, 5 mm) could be added to this water, could be agitated for 5 minutes, and were distributed.
[0024]To this dispersed matter, as matrix resin Subsequently, 87.5 g of polyethylene succinate resin powder (mean particle diameter of 32 micrometers), After adding 6 g of solid acrylic polymer latex, it was made to condense by adding gradually 0.5% of the weight of positive ion flocculating agents [63 g of] (the product made by Betz Laboratories, and trade name:Betz 1260), and the slurry was obtained.
[0025]This slurry is added to the sheet machine [Kumagaya Riki Kogyo K.K. make] containing 17.5 l. of water, The sheet which obtained the sheet which dried and became wet on a 0.18-mm screen, and was subsequently obtained was compressed lightly, and the hemp fiber strengthening aliphatic-polyester-resin composite sheet was obtained by making it dry at 60 ** and removing water. At this time, hemp fibers were 100 weight sections to aliphatic-polyester-resin 100 weight section.
[0026]Two sheets of this sheet were laminated and the compressed sheet of base weight 580 g/m2 was obtained by cooling at 140 ** under the pressure of 20 kg/cm2, and cooling at 40 ** under power at the same pressure after application-of-pressure heating.
[0027]When the tensile test which applied the obtained sheet to JIS K7127 correspondingly was done, the tensile strength of 4.4kg[/mm] 2 was shown. In the heat resistance of the obtained sheet, when heat deflection temperature was measured according to JIS K7207, the result of 101.3 ** of having excelled was obtained.
[0028]Instead of example 2 hemp fiber, 87.5 g of rayon fibers (made by the Yamato ** Co. 7d x 3 mm), Except for using 87.5 g of polybutylene succinate textiles (85d x 3 mm) instead of polyethylene succinate resin powder, the compressed sheet of base weight 580 g/m2 was obtained completely like Example 1. When the tensile test of this sheet was done, the tensile strength of 4.1kg[/mm] 2 was shown. When heat resistance of the obtained sheet was performed under the same conditions as Example 1, the result of 116.8 ** in heat deflection temperature of having excelled was obtained.
[0029]When polyethylene succinate resin powder used in comparative example 1 Example 1 was used as the film by heat pressing and the same tensile test as Example 1 was done, it was the intensity of 2.5kg[/mm] 2. When heat resistance of the obtained sheet was performed under the same conditions as Example 1, the result of 69.7 ** in heat deflection temperature was obtained.
[0030] [Effect of the Invention]By composite-izing the heat-resistant high biodegradable fiber for strengthening represented by aliphatic polyester with biodegradability, and the natural fiber according to this invention, The intensity of aliphatic polyester and heat resistance can be raised by leaps and bounds, It has sufficient intensity within the period when the purpose of use should be achieved when used in natural environment, after the purpose of use is achieved, it is decomposed by the microorganism in natural environment, and it becomes possible to provide the biodegradable fiber strengthening Plastic solid which can be extinguished.